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by

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Magnetic Susceptibility and Ligand-Field Theory

Juan Padilla[+] and William E. Hatfield*

Abstract

Magnetic susceptibility data for praseodymium, neodymium, gadolinium, holmium, and erbium phthalocyanines taken in the temperature ranges 80-300 K or 4.2-300 K are reported. The σ- and π-interactions of the pyrrolic nitrogen ligand with the praseodymium, neodymium, holmium, and erbium f-orbitals were obtained from angular overlap model ligand-field calculations including the full ground-state manifold. The position of the pyrrolic nitrogen ligand in the metallic two-dimensional spectrochemical series is reported. The results show that the pyrrolic nitrogen is a weak σ-donor and a moderate π-donor ligand. The cross-term AOM parameter $\theta_{\pi\sigma}$ is necessary in order to get good fits.

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Introduction

Following the synthesis of the lanthanide phthalocyanines[1] much attention has been focussed on their chemical and physical properties such as spectroscopic characterization[2], electrical resistivities,[3,2(n)] thermal stability,[4] magnetic properties,[5, 2(g), 2(j),2(l),2(m),2(r),3(g)], electrochromism,[2(f),6,2(j),2(l),2(o),2(p),2(q)] solubility,[7] electrocrystallization,[2(i)] and X-ray structures.[2(i),8] However, no theoretical models have been applied for the explanation of the energetic effects of the ligands upon the lanthanide ion. The angular overlap model (AOM)[9] permits the quantitative determination of the relative magnitude and the sign of the σ- and π-interactions of ligands with metal ions. This feature of AOM brings the concept of functional groups to ligand-field theory.

Because the AOM is a parametric model, it is necessary to adjust certain parameters to experimental values. Absorption spectroscopy (UV-Vis-IR) provides an experimental tool to obtain the σ and π interactions between ligands and metals. They can be calculated from the transition energies, and the interpretation accomplished using the AOM. However, in the case of lanthanide phthalocyanines, such studies are difficult for two reasons. First, the f-f transitions are parity forbidden and therefore of weak intensity. Secondly, the $\pi \rightarrow \pi*$ bands of the macrocycle phthalocyanine are intense, and obscure the weaker f-f bands which are required for the analysis. This obstacle may be overcome with help of magnetic susceptibility measurements.

In this work, magnetic susceptibility measurements (80-300 K or 4.2-300 K) were used to determine the AOM parameters of praseodymium, neodymium, holmium, and erbium phthalocyanines. Also, the positions of the compounds in the metallic two-dimensional spectrochemical series were determined.

Experimental Section

Synthesis. The lanthanide phthalocyanines, H(Pc)Ln(Pc) [Pc = dianion phthalocyaninato, Ln = Pr, Nd, Gd, Ho, and Er], were prepared by a modification of the synthesis described in the literature[2(a)] by reacting an excess of 1,2-dicyanobenzene with the appropriate lanthanide acetate, and further chromatographic separation and purification. The modification consisted of subliming, before the chromatographic separation, under vacuum at 300°C overnight several times (2-4) until no more sublimated material was collected from the cold finger. The sublimation eliminates most of the 1,2-dicyanobenzene that did not react, and its decomposition products. The dark blue phthalocyanines collected from the chromatographic column were used in this study. The purity of the samples was checked by UV-Vis, IR, and EPR spectra.

Magnetic Susceptibility Measurements. Temperature-dependent data used in the fittings were collected with a Faraday balance in the 80-300 K range, and with a vibrating sample magnetometer in the 4.2-80 K range. The instruments were calibrated using a standard of $Hg[Co(SCN)_4]$. Diamagnetic corrections were calculated using Pascal's constants.[10]

Results and Discussion

Curie-Weiss Fits. Curie-Weiss fits of the magnetic susceptibility data yielded the best-fit parameters given in Table 1. The Weiss constants for praseodymium and neodymium phthalocyanines are rather large compared with the values obtained for gadolinium, holmium, and erbium phthalocyanines, which are in closer agreement with the Curie law. There are three possible explanations account for the differences; either the lanthanide ions show cooperative phenomena, or the temperature independent paramagnetism (TIP) is not negligible, or there are accessible low-lying magnetic states. The negative sign for the Weiss constants suggests an antiferromagnetic exchange coupling; however, in such cases it has been observed that the Neel temperature, T_N, is approximately equal to the negative of the Weiss constant ($\theta = T_N$).[11] That means the magnetic ordering should be observed near 110 and 61 K for praseodymium and neodymium phthalocyanines, respectively. Magnetic susceptibility measurements collected down to 4.2 K however show no indication of exchange coupling, thus ruling out cooperative magnetic phenomena.

TIP arises from the mixture into the ground state of thermally non-populated, yet low lying excited states.[12] Of the five lanthanide ions considered in this study, praseodymium and neodymium are the ones with the lowest lying first excited states (see Table 1), and hence the ones that more likely could show appreciable TIP.

Even after making the corrections to account for the TIP,[10a] the corrected Weiss constants are still different from the free-ion values, which is indicative of the influence of the ligand-field. It is important to remember that even ligand-field effects in lanthanide compounds represent only small perturbations from the point of view of electronic spectroscopy. The states that arise are the essence of their magnetic properties.

Angular Overlap Model Fits. The AOM calculations involved the diagonalization of the complete ground state manifold of the free-ion basis under the ligand-field potential, and a subsequent computation of magnetic susceptibilities by perturbation theory within the Van Vleck equation using Racah's irreducible tensor operator techniques.[13]

The theoretically calculated magnetic susceptibility was fit to the experimental data by using the nonlinear least-squares fitting routines SIMPLEX,[14] or GRADX.[15] Similar results were obtained independently using both routines. The criterion of best-fit was the minimization of the function:

$$F = \Sigma (x_i^{obsd} - x_i^{calcd})^2 / (x_{i\,obsd})^2 \qquad .$$

Since the energy gaps between the free-ion ground states and their first excited states of praseodymium, neodymium, holmium, and erbium ions (see Table 1) are large compared with kT (= 205 cm^{-1} at room temperature), the ground-state manifold

wavefunctions should suffice to give an excellent account of the susceptibilities. It has been found such approximation has a negligible influence on the magnetic moments, and will lead to errors of less than 0.1 B.M.[16]

The ground-state energy splittings obtained from the diagonalization of the ligand-field energy matrix for praseodymium, neodymium, holmium, and erbium phthalocyanines are 344, 483, 2200, and 2940 cm^{-1}, respectively. The energy splittings of praseodymium and neodymium phthalocyanines are of the same order of magnitude as the thermal energy at room temperature, and therefore, all the levels are expected to be populated at high temperatures. By contrast, the energy splittings for holmium and erbium phthalocyanines are more than one order of magnitude larger than kT, so only the low lying energy levels are expected to be appreciably populated.

The low energy transitions lie in the far-Ir or IR range of the spectrum, and the ligand-field parameters could not be fit using the experimental data from the far-IR or IR spectra of lanthanide phthalocyanines because the f-f transitions are parity forbidden, therefore of very weak intensity, and they could not be detected from the spectra.

The AOM best-fit parameters are listed in Table 2. It was not possible to get good fittings when the cross-term parameter was not included. This is not an unexpected result since it is generally found in chelate compounds.[17] The cross-term parameter represents the degree of admixture between the σ- and π-orbitals in the nitrogen atoms, since in the lanthanide phthalocyanines

the nitrogen σ-orbital is not directly pointing towards the lanthanide ion. This is the so-called misdirected valency contribution to the ligand-field potential, and it was taken into consideration by adding the extra terms Y_2, Y_4, and Y_6 in the ligand-field spherical harmonics expansion.

It was possible to get good fittings with slightly different sets of AOM parameters. This was particularly noticeable in the case of praseodymium phthalocyanine; e_σ may change within the 107-127 cm^{-1} range; e_π in the 44-25 cm^{-1} range, and $e_{\pi\sigma}$ in the 10-25 cm^{-1} range. The fits in this region were very good (the error was less than 3%).

Compared with the behavior observed during the fitting of praseodymium phthalocyanine, in the case of neodymium, holmium and erbium phthalocyanines the range of values of AOM parameters for which a good fit is possible is narrower. The quality of the fitting worsens considerably for values outside the best-fit range. Also, no clear correlation among the AOM parameters could be detected. These observations support the idea of unique fittings.

When the parameter e_π was included, the quality of fits fell off very rapidly indeed for $e_\pi = 0$, and the assumption that the π-bonding between nitrogen and lanthanide in the plane of the sp2 hybrid is negligible was apparently justified. The final situation was that there exists a narrow region in polyparameter space in which all the AOM parameters fit well, and going outside that region even a small way reduced the quality of the fit significantly.

The best-fit values for e_σ are rather small compared to the values usually obtained for transition metal ions (on the order of a few thousand wavenumbers). This may be considered as a reflection of the screening effect that occurs in the lanthanide series, and of the weak covalency of the Ln-N bond. The parameter e_σ did not affect the magnetic susceptibility very much as this affected mainly the gross splitting in the ground manifold, i.e., spectral properties, with the lower levels being populated to a greater extent, and those populated levels determine the magnetic properties for the most part.

Positive e_π's imply π donation from the ligand to metal, and negative ones π acceptor properties of the ligand. From the fittings, it was found e_π to be greater than the ideal value of 0.25 e_σ predicted from simpler approaches. The fact that e_π turned out to be greater than the ideal value is indicative of a relatively strong π-interaction. The donor properties of the pyrrolic nitrogen atom seems likely even given a delocalized system such as exists here. In the pyrrole ring, the delocalization in the imine group seems to be quite small, and little disruption is caused by π-donation.

The value e_π of zero shows that the electrons in the sp^2 hybrid bonding the imine nitrogen are not in a position to interact with the lanthanide ions, confirming the initial supposition.

Figure 1 shows the position of praseodymium, neodymium. holmium, and erbium phthalocyanines in the metallic two-dimensional spectrochemical series. The parameters e_σ and e_π

increase somewhat as the lanthanide ionic radii decrease. The trends may be rationalized considering the Ln-N bond lengths (and the Pc-Pc intraring separation distances) decrease, increasing the orbital overlap, and strengthening the bonds.

Conclusions

The advantage of using a series of closely related lanthanide phthalocyanines is that such a study permits the determination of trends in the AOM parameters, and these may be related to chemical features of the complexes. It has been assumed by various authors that the AOM parameters are transferable from one compound to another. The order observed for the σ-bonding is e_σ (Pr) < e_σ (Nd) < e_σ (Ho) < e_σ (Er), and the same trend is observed for π-bonding. This clearly indicates a direct relationship between the σ- and π-bond strengths, and the lanthanide-nitrogen bond distances. The effect leads to the conclusion that no discussion of transferability of the AOM parameters is possible unless the bond length distances are known.

From this analysis, it has been found that the AOM parameters may be associated with local interactions of the lanthanide ion and its individual ligands. Us of the AOM has allowed the introduction, explicitly, of the notion of chemical functional groups to ligand-field theory. The AOM e_σ and e_π parameters show that the pyrrolic nitrogen atom acts as a weak σ-donor and a moderate π-donor ligand. The position of the praseodymium, neodymium, holmium, and erbium phthalocyanines in

the metallic two-dimensional spectrochemical series has been determined for the first time (Figure 1).

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Figure Caption

Figure 1. Position of lanthanide phthalocyanines in the metallic
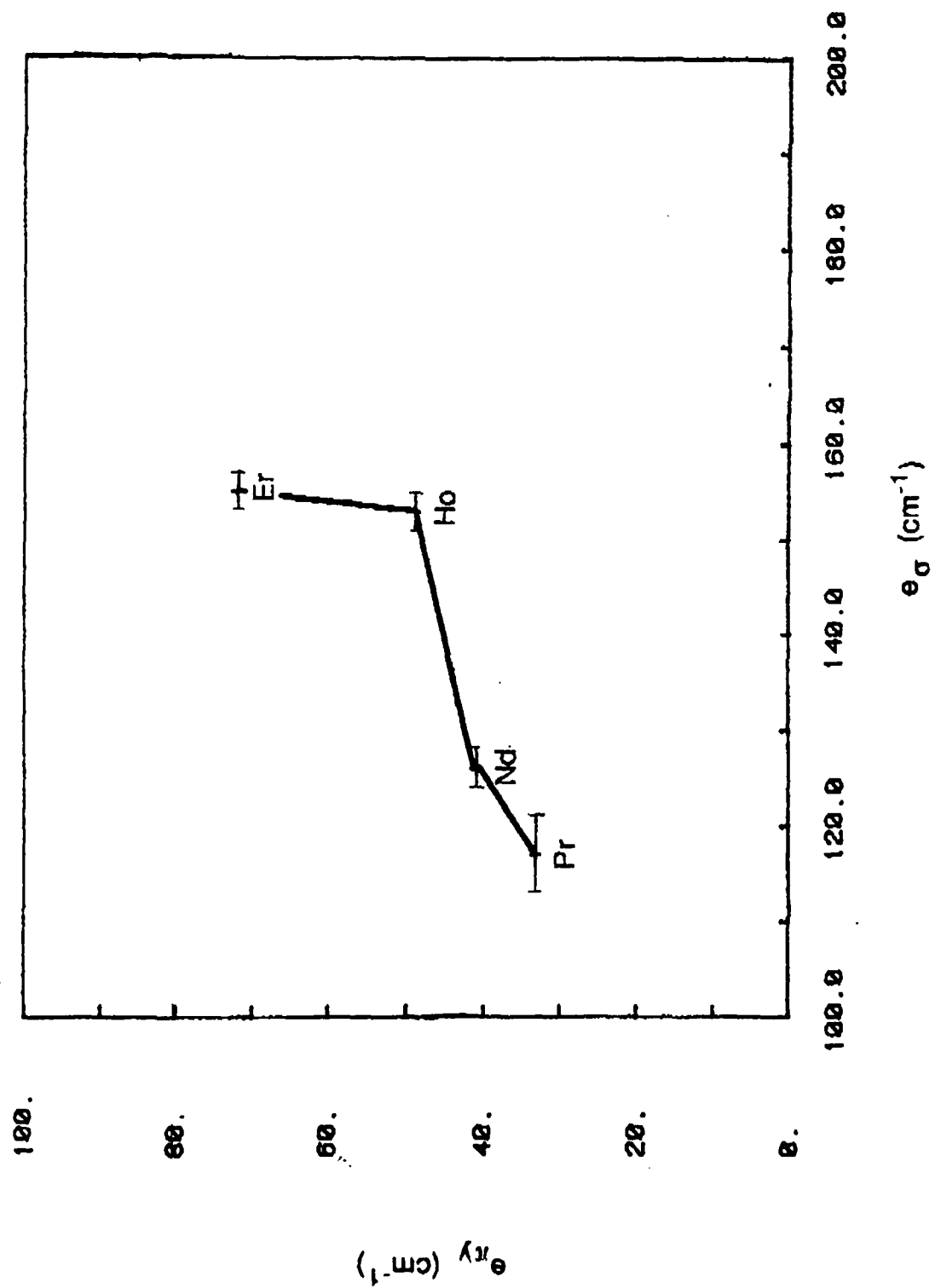two-dimensional spectrochemical series.

Table 1. Curie-Weiss best-fit parameters of lanthanide phthalocyanines, and the separation energy between the ground state and the first excited state of the free-ion lanthanides.

Compound	C(Emu K mole$^{-1)}$	θ (K)	ΔE (cm^{-1})
H(Pc)Pr(Pc)	1.90	-110	2,150
H(Pc)Nd(Pc)	1.17	-61	1,900
H(Pc)Gd(Pc)	6.61	6	30,000
H(Pc)Ho(Pc)	13.00	0	5,200
H(Pc)Er(Pc)	8.83	4	6,500

Table 2. AOM best-fit parameters in wavenumbers, and percent errors between the theoretically calculated magnetic susceptibilities and the experimental data.

Parameter	H(Pc)Pr(Pc)	H(Pc)Nd(Pc)	H(Pc)Ho(Pc)	H(Pc)Er(Pc)
e_σ	117	126	153	155
e_π	33	41	49	72
$e_{\pi\sigma}$	10	10	12	2
e_π/e_σ	0.28	0.33	0.32	0.46
% Error	2.8	2.0	0.8	3.2

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